

Theoretical Study of the Structure and Reactions of Uranium Fluorides

Bárbara M. T. C. Peluzo, Breno R. L. Galvão

Chemistry Department, Centro Federal de Educação Tecnológica de Minas Gerais, Av. Amazonas 5253, Belo Horizonte, Brasil

Abstract:

Uranium is an actinide metal mostly known for its use as fuel at nuclear power plants. Once the amount of fissile isotope (^{235}U) in nature is not enough for a chain reaction, uranium must be enriched in order to achieve roughly 4% of the 235 isotope. Therefore, it is converted into UF_6 , a gaseous compound, which can be used in isotope separation techniques (being centrifugation the most used and laser enrichment a promising one) ¹. Currently UF_6 is made by $\text{UF}_4(\text{s})$ fluorination, a reaction which presents sub-products. An example of related reaction is UF_6 successive reduction by hydrogen, leading to lower uranium fluorides and HF ^{2,3}.

In this work, a DFT study has been performed on 3 uranium fluorides and their reactions in gas phase, covering the most stable equilibrium geometry and spin multiplicities. We used the basis sets TZP-DKH for fluorine and hydrogen and LANL2DZ/ECP for uranium. The DFT functional chosen was the hybrid one PBE0.

Initial optimization calculations lead to two isomers (C_{2v} and D_{2d}) for UF_4 ; C_{4v} symmetry for UF_5 and O_h , for UF_6 . After that, it has been investigated possible transition states (TS) for UF_6 formation via reaction between UF_4 and F_2 . It has been employed a Linear Least Motion (LLM) analysis for this TS search, followed by geometry optimizations. Two TS had been obtained, been one of them the structure which connects the minima $\text{UF}_4 + \text{F}_2$ and UF_6 . This reaction mechanism has been studied in detail using Intrinsic Reaction Coordinate (IRC) calculations.

Another reaction studied was UF_6 synthesis via UF_4 and HF, a reaction that occurs in two steps and presents UF_5 as intermediate compound. In the calculations performed, it has been found a TS which consists of a UF_5 (D_{3h}) molecule and a hydrogen atom as a ligand. IRC calculations showed a different product, the complex UF_5H , which had been observed by Eerkens ⁴. Besides this, it has been obtained the infrared spectra of this product, which had not been theoretically or experimentally observed yet.

Vibrational frequency calculations have also been performed for the fluorides and they present good agreement with experimental data available. Finally, we have performed



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an investigation on possible isotopic shifts at the vibrational spectra of 6 UF_6 isotopologues, i.e., compounds whose compositions differ by an isotope. As a result, it has been found isotopic shifts for the frequencies ν_3 and ν_4 , which may be used in uranium isotopic separation, since all species presented slightly different frequencies, mainly at ν_3 . Same calculations have been performed for UF_5H and shifts were found at ν_{10} .

Key-words: UF_6 . DFT. potential energy surface. isotopic shift.

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